



## Color changes in fish during grilling – Influences of heat transfer and heating medium on browning color

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### ABSTRACT

Samples of red sea bream (*Pagrus major*) were grilled under radiant (far-infrared radiation, FIR) and convective (superheated steam, SHS) heating. The temperature and color (CIE  $L^*$ ,  $a^*$ , and  $b^*$  values) of the sample surface were monitored over time, using SHS, dry air, and  $N_2$  as heating media. The rate of  $L^*$  changes was evaluated by treating the browning reaction as first-order. Color changes based on  $a^*$  and  $b^*$  values were effectively correlated with the  $L^*$  value, using empirical equations. A slower reduction in  $L^*$  for heating with SHS rather than FIR was obtained, probably because of different activation energies (31.5 and 50.7 kJ mol<sup>-1</sup>) and frequency factors (8.2 and 4759 s<sup>-1</sup>). The order of reductions in  $L^*$  was dry air >  $N_2$  = SHS. The absence of  $O_2$  in the heating medium could be the reason for the delay in the browning reaction during heating using  $N_2$  and SHS.

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### 1. Introduction

The challenge of developing advanced thermal processes for the food industry continues, in line with the demand for enhanced food safety and quality, because thermal processing is always associated with some undesirable degradation of heat-sensitive quality attributes. Quality degradation as a result of excessive heating, especially at high temperatures, and its prevention require individual attention. The effect of thermal processing on sensory quality in marine products is difficult to predict because of intra- and inter-specific differences in fish species and factors such as appearance, odor, color, flavor, and texture.

Consumers often assess the initial quality of a product by its color and appearance, and color serves as a clue as to how well food is cooked. The analysis of color changes during heating therefore has a great influence not only on the quality but also on the safety of food products. Using a color difference meter, a sensor that touches the food, color is determined by measuring the reflection of emitted light. Several researchers have contributed to this field (Kaida et al., 1999; Pedreshi et al., 2006; Kong et al., 2007; Yan et al., 2008; Braeckman et al., 2009). Moreover, if the changes in food color, including the browning process, during cooking can be predicted and effectively modeled, appropriate cooking methods such as grilling can be improved. For grilling processes in the food industry, conduction and convective heat transfer have

mainly been used, as well as radiant heat transfer, e.g., from an infrared (IR) lamp (Sakai and Mao, 2006). Shibukawa et al. (1989), Sato et al. (1992), and Sugiyama et al. (1993) reported the influence of surface color on browning formation, as well as the influence of the ratio of radiant heat transfer to the radiation wavelength on scorching color. After comparing food cooked in a convection oven and that cooked in a radiation oven, Sato et al. (1992) claimed that the heat transfer system did not directly affect the browning color. However, the heat transfer system influences the surface temperatures of foods, and surface temperature differences affect the browning color.

Recently, superheated steam (SHS, steam-spray type) has been widely used as a heat source in steam convection ovens in hotels, kitchens, and elsewhere. A steam convection oven features high reproducibility and can process large amounts of food. The characteristics of fish grilled by SHS and by propane-gas heating were compared by Hamada et al. (2006). They obtained better results with the former than with the latter; in particular, the samples were juicier in the former case and the grilling time was shorter. Ohishi and Shibukawa (2008) found that a cake baked in an SHS oven was darker than a cake baked in a steam-free convection oven, indicating a shorter baking time. They observed a considerable transfer of heat during the initial stage of heating in an SHS oven.

Developing a kinetic model of food color changes during cooking is an important challenge in food processing. If the rate and temperature dependence of a reaction are known, they can, in principle, be predicted and therefore controlled (Martins et al.,

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## Nomenclature

$E_a$	activation energy (kJ mol <sup>-1</sup> )	<i>Subscripts</i>	
$k_0$	frequency factor (s <sup>-1</sup> )	<i>c</i>	calculated
$R$	molar gas constant (J K <sup>-1</sup> mol <sup>-1</sup> )	<i>f</i>	final
$t$	grilling time (s)	<i>i</i>	initial
$T$	surface temperature (K)	<i>m</i>	measured
$Y$	dimensionless parameter related to color lightness (-)	<i>cs</i>	calculated at same surface temperature
$a^*$	fish surface color position on red/green axis (-)	<i>msi</i>	measured at similar surface temperature
$b^*$	fish surface color position on blue/yellow axis (-)		
$L^*$	fish surface color lightness (-)		

2001). In the browning of bakery products, the model suggested by Broyart et al. (1998) for the baking of crackers is widely used. They proposed a non-isothermal kinetics approach to modeling color development on the food surface during baking; in the model, the thermal history and moisture content are taken into account. With fish, however, obtaining the water activity (or moisture content) variation during grilling is complicated. Such measurements require the setting up of a destructive method for accurate sampling while the fish is still hot and deformable, and water losses by evaporation from cut surfaces must be minimized (Wagner et al., 2007; Purlis and Salvadori, 2009).

Onishi et al. (2011) evaluated the browning on the surface of baked bread using computer vision, numerical simulations, and non-isothermal kinetics, and modeled the development of browning color formation. They did not consider weight loss as a factor in their model, because they found a high correlation between weight loss and the CIE  $L^*$  value only at the highest baking temperature, that is, within the temperature range where browning ends and initial carbonization begins. Nakamura et al. (2011) analyzed the browning of fish samples during grilling on the basis of the relationships among color, sample surface temperature, and grilling time using near-IR (NIR) heating. The proposed method enabled prediction of the  $L^*$  value from the surface temperature history, as well as the CIE  $a^*$  and  $b^*$  values, from empirically developed equations obtained using an NIR heating grill, and thus enabled the characteristic trajectory of color changes for grilled fish in colorimetric space ( $L^*$ ,  $a^*$ , and  $b^*$ ) to be drawn. However, there are very few reports on the effects of other heat transfer modes during grilling processes, or on the differences among various heating media in browning color simulation.

In the present study, we examined the influence of the heating medium used for grilling on browning color formation in fish, using two different heat transfer systems, namely radiant (far IR, FIR) and convective (SHS) heating, and three convective heating media: SHS, dry air, and nitrogen (N<sub>2</sub>).

## 2. Materials and methods

### 2.1. Raw material

Red sea bream (*Pagrus major*), a white-flesh fish (cultivated in Ehime, Japan), was used as the sample material. Raw fillets were purchased on the day of the experiment. The skin and bones were removed, and the fillets were cut into pieces of size 5 × 6 × 2 cm<sup>3</sup> (width × length × thickness) for all the experiments. The samples were wrapped in wrapping film and refrigerated (5 °C) until they were used in the experiments. The initial moisture content of the samples was approximately 77% w/w (wet basis).

### 2.2. Experimental conditions

Two experimental apparatuses were used to evaluate the color changes of the samples during grilling under different heat transfer

systems: an FIR oven (radiant) and a convection-type oven (convective). Schematic diagrams of these apparatuses and their heating sources (manually assembled oven, laboratory-scale) are shown in Fig. 1A and B for FIR heating (100 V/750 W) and convection-type heating (steam-spray type), respectively.

#### 2.2.1. FIR-type oven

The FIR heater (electric ceramic plate heater PLC-328, Noritake Co., Aichi, Japan) was square in shape (12 × 12 cm<sup>2</sup>). The IR energy was irradiated downward from the heater. The samples, which were positioned approximately 8 cm below the heat source, were placed on an electronic balance. The radiation energy, measured by a radiation sensor (RF30 Captec, Villeneuve d'Ascq, France) at the sample position, was 2.7 × 10<sup>4</sup> W m<sup>-2</sup>. Sampling of the grilled samples was conducted at prescribed times of 0, 2, 4, 6, 8, and 10 min.

#### 2.2.2. Convection-type oven

Fish samples that were similar in shape and size to those used in the FIR experiments were prepared in the same manner as described above. Three heating media were tested: SHS, dry air, and N<sub>2</sub>. The samples were positioned approximately 8 cm below the hot-gas outlet. In the case of SHS, steam was generated by a boiler and superheated from 100 °C to 240 °C by gas heating. The steam was sprayed onto the sample at a flow rate of 2.5 kg h<sup>-1</sup>. Dry air or N<sub>2</sub> was injected via a pipe connected to the super-steamer (see Fig. 1B), instead of via a direct pipe connection to the steam boiler, as in the case of SHS.

To compare the heating media used in this oven, similar surface temperature histories were used for the three heating media. Although the internal oven temperature was set at 200 °C (in all cases), SHS was sprayed at 200 °C–240 °C with a flow velocity of 27.4 m s<sup>-1</sup>, whereas dry air was sprayed at 200 °C–220 °C with a flow velocity of 15 m s<sup>-1</sup>. For the experiments with N<sub>2</sub>, the conditions were similar to those used for dry air. Sampling of the grilled samples for color and surface temperature measurements was conducted at prescribed times of 0, 1, 2, 4, 6, 8, 10, 12, and 14 min.

### 2.3. Surface temperature measurements

The surface temperatures of the samples were measured using a K-type thermocouple ( $\phi = 0.5$  mm). A personal computer, a data-logger (Thermodac 5001A, Eto Denki Co., Tokyo, Japan), and software (Thermodac-E/Ef 2.6, Eto Denki Co.) were used to collect the temperature data.

To justify the use of K-type thermocouples instead of IR sensors, recognized as a more robust device for surface temperature measurements, the accuracy of the surface temperature profiles collected using K-type thermocouples was verified by comparison with profiles collected with IR sensors, using SHS heating under the conditions described above, and in the temperature range 110–150 °C. The surface temperature profiles were similar, with a variation of ±0.5 °C in the worst case. In the comparison of the

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